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Solid and Solution Structural Studies of Dimeric and Tetrameric Molybdenum(VI) Malate Complexes①

ZHANG Rong-Hua ZHOU Zhao-Hui② WAN Hui-Lin
(*Department of Chemistry, College of Chemistry and Chemical Engineering, State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen* 361005, *China*)

ABSTRACT Reactions of potassium molybdate with racemic malic acid (H_3mal = $C_4H_6O_5$) result in the isolation of two mesomeric molybdenum malate complexes $K_8[(MoO_2)_2O(R\text{-mal})_2][(MoO_2)_2O(S\text{-mal})_2]\cdot 4H_2O$ **1** and $(Him)_2K_6[(MoO_2)_4O_3(R\text{-mal})_2][(MoO_2)_4O_3(S\text{-mal})_2]\cdot 8H_2O$ **2**. Complex **1** belongs to the monoclinic system, space group $C2/c$ with a = 14.8637(3), b = 6.9544(1), c = 19.6783(5) Å, β = 100.081(2)°, V = 2002.70(7) Å^3, M_r = 1452.88, Z = 2, F(000) = 1416, T = 173 K, D_c = 2.409 g/cm^3, μ(Mo$K\alpha$) = 2.167, R = 0.0283 and wR = 0.0733. **2** is of triclinic system, space group $P\bar{1}$ with a = 8.7707(2), b = 9.3310(3), c = 17.9093(7) Å, α = 83.781(3), β = 85.626(2), γ = 84.822(2)°, V = 1447.84(8) Å^3, M_r = 2160.68, Z = 1, F(000) = 1048, T = 173 K, D_c = 2.478 g/cm^3, μ(Mo$K\alpha$) = 2.230, R = 0.0234 and wR = 0.0584. **1** is the first isolated dinuclear molybdenum(VI) malato complex in 1:1 molar ratio. The molybdenum atoms in the two complexes are six-coordinated in an approximately octahedral geometry. Two malates coordinate tridentately with the Mo atom *via* their α-alkoxy, α-carboxy and β-carboxy groups in **1** and **2**. β-Carboxy group in **2** further links with the other two Mo atoms to give a tetrameric unit. The solution ^{1}H and ^{13}C NMR spectra indicate that dimeric malate molybdenum in **1** dissociates partly in solution and exists in an equilibrium with tetrameric species, while **2** is stable and retains its tetrameric structure without any dissociation.

Keywords: molybdate(VI), malate, nitrogenase, crystal structure, NMR

1 INTRODUCTION

Nitrogenases catalyze the conversion of atmospheric dinitrogen to bioavailable ammonia in biological nitrogen cycles. High-resolution structural studies of nitrogenases have revealed the active site of FeMo-co as a cage-like $MoFe_7S_9X$-*R*-homocitrate cluster[1, 2]. The cluster binds the substrate N_2 and catalyzes the inert N_2 triple bond to form NH_3[3, 4]. Within the cluster, the molybdenum atom is surrounded by three sulfur atoms, a nitrogen atom from the imidazolyl group of a histidine residue, and two oxygen atoms from α-alkoxy and α-carboxy groups of *R*-homocitrate. The interstitial atom X (X = O, N or C) makes the six central Fe atoms of FeMo-co coordinated saturated[5 ~ 7]. This leads to the support of the notion that the Mo atom is directly involved in the nitrogen reduction[8 ~ 10]. Early studies have shown that in vitro biosyntheses of FeMo-co with alternative polycarboxylates (*i.e.*, citrate, malate, citramalate, *cis*-aconitate) resulted in the lower nitrogen fixing ability than that with homo-

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② Corresponding author. Tel.: +86-592-2184531, E-mail: zhzhou@xmu.edu.cn

citrate; however, they remained capable of reduction from C_2H_2 to C_2H_4[11 ~ 13]. Moreover, it has been suggested that a possible function of the tricarboxylic acid in the biosynthesis of the cofactor of nitrogenase is to mobilize molybdenum or vanadium from the appropriate storage enzyme[14, 15]. Molybdenum or vanadium is believed to be taken up by the organisms as MoO_4^{2-} or VO_4^{2-} [16 ~ 21]. The coordination chemistry of molybdenum(VI) is thus important in the transport of molybdenum from its natural aqueous environment into its ultimate form in biological systems[22]. This has motivated studies and elucidation of the interactions between molybdenum and α-hydroxycarboxylic acids.

H_3mal is one of the α-hydroxycarboxylic acids present in human plasma and is heavily involved in the citric acid cycle[23, 24]. Formations of molybdenum malate have been studied in different pH ranges by polarimetry, potentiometry, spectrophotometry, enthalpimetric titration and NMR spectroscopy[25 ~ 27]. And some typical stoichiometries such as 2:1, 1:1 and 1:2 for the molybdate to malate ratio have been proposed. The structurally characterized malato molybdates with 2:1 and 1:2 ratios (Mo:mal) were reported as $(NH_4)_4[Mo_4O_{11}(S\text{-mal})_2]\cdot 6H_2O$[28 ~ 30], $(NH_4)_4[Mo_4O_{11}(R\text{-mal})_2]\cdot 6H_2O$[31], $Cs_2[MoO_2(S\text{-Hmal})_2]\cdot H_2O$[32], $Na_3[MoO_2H(S\text{-mal})_2]$, $K_3[MoO_2H(S\text{-mal})_2]\cdot H_2O$[33] and $(NH_4)_4[MoO_2(S\text{-mal})_2][MoO_2(R\text{-mal})_2]$[34]. However, there is no previous assignment of the species in 1:1 ratio. In this work, we report the isolation, spectroscopic and structural characterization of a new dinuclear molybdenum(VI) malate complex, $K_8[(MoO_2)_2O(R\text{-mal})_2][(MoO_2)_2O(S\text{-mal})_2]\cdot 4H_2O$ **1**, and a tetrameric molybdenum(VI) malate complex, $(Him)_2K_6[(MoO_2)_4O_3(R\text{-mal})_2][(MoO_2)_4O_3(S\text{-mal})_2]\cdot 8H_2O$ **2**.

2 EXPERIMENTAL

2. 1 Materials and general methods

Malate was used as both reactant and buffer agent. The pH value was measured with the potentiometric method with a digital PHB-8 pH meter. Infrared spectra were recorded as Nujol mulls using a Nicolet 200 FT-IR spectrometer. Elemental analyses were performed using Vario EL III elemental analyzer. NMR data were recorded on a Bruker Avance II (400 MHz) spectrometer using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the internal reference. *R,S*-Malic acid (99%) was obtained from Sigma and used without further purification.

2. 2 Synthesis of $K_8[(Mo_\Lambda O_2)_2O(R\text{-mal})_2][(Mo_\Delta O_2)_2O(S\text{-mal})_2]\cdot 4H_2O$ 1

R,S-malic acid (1.34 g, 10 mmol) was added to a stirred solution of potassium molybdate pentahydrate ($K_2MoO_4\cdot 5H_2O$, 3.28 g, 10 mmol) in water (10 mL). The mixture (pH = 4.8) was heated in a water bath at 70 °C for four days. Compound $K_8[(MoO_2)_2O(R\text{-mal})_2][(MoO_2)_2O(S\text{-mal})_2]\cdot 4H_2O$ **1** was crystallized out, and then filtered, washed with water and air dried to yield white crystals (1.25 g, 49%). ^{1}H NMR (400 MHz, D_2O, 25 °C, DSS): δ = 4.95 (s, 4H; CH), 2.83～2.60 ppm (m, 8H; CH_2); ^{13}C NMR (100 MHz, D_2O, 25 °C, DSS): δ = 187.7, 181.2, 84.7, 41.3 ppm; IR (KBr): 3427(s), 1639(vs), 1583(vs), 1393(vs), 1363(m), 1084(m), 925(vs), 908(s), 891(vs), 876(s), 841(m), 723(s), 610(m), 548(vs) cm^{-1}. Anal. Calcd. (%) for $C_{16}H_{20}K_8Mo_4O_{34}$: C, 13.2; H, 1.4. Found (%): C, 13.6; H, 1.4.

2. 3 Synthesis of $(Him)_2K_6[(Mo_\Lambda O_2)_4O_3(R\text{-mal})_2][(Mo_\Delta O_2)_4O_3(S\text{-mal})_2]\cdot 8H_2O$ 2

R,S-malic acid (0.27 g, 2 mmol) and imidizole (0.068 g, 1 mmol) were added to a stirred solution of $K_2MoO_4\cdot 5H_2O$ (1.31 g, 4 mmol) in water (50 mL). The pH of the reaction mixture was carefully adjusted to 3.0 by adding diluted HCl. The mixture was heated in a water bath at 80 °C for six days. Compound **2** was crystallized out; after that it was filtered, washed with water and air dried to yield white crystals (0.50 g, 46%). ^{1}H NMR (400 MHz, D_2O, 25 °C, DSS): δ = 8.72 (s, 2H; CH=N, im), 7.50 (s, 4H; CH=C, im), 4.99 (dd, J = 2.0 and 1.6 Hz, 4H; CH), 3.06～2.90 ppm (m, 8H; CH_2). ^{13}C NMR (100 MHz, D_2O, 25 °C, DSS): δ = 186.4, 182.0, 136.2, 121.7, 82.2, 42.3 ppm. IR (KBr): 3472(s), 3127(m), 1657(s), 1625(s), 1587(vs),

1433(m), 1427(m), 1396(s), 1084(m), 933(vs), 905(vs), 876(s), 801(m), 713(s), 634(s), 568(s), 504(m) cm^{-1}. Anal. Calcd. (%) for $C_{22}H_{38}K_6Mo_8N_4O_{50}$: C, 12.2; H, 1.8; N, 2.6. Found (%): C, 12.4; H, 1.9; N, 2.6.

2. 4 Structure determination

Data collections of **1** and **2** were performed on an Oxford Gemini S Ultra system with Mo$K\alpha$ radiation (λ = 0.71073 Å) at 173 K. Absorption corrections were applied by using the program CrysAlis (multi-scan). Structures were primarily solved by WinGX package[35] and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms using SHELXL-97[36]. Hydrogen atoms were included and located from difference Fourier map but not refined anistropically. Crystal data collection and refinement parameters are summarized in Table 1. Selected bond lengths and bond angles are listed in Tables 2 and 3, respectively.

Table 1. Crystallographic Data for 1 and 2

	1	**2**
Empirical formula	$C_{16}H_{20}K_8Mo_4O_{34}$	$C_{22}H_{38}K_6Mo_8N_4O_{50}$
Formula weight	1452.88	2160.68
Crystal color	Colorless	
Crystal size (mm)	0.20 × 0.18 × 0.05	0.20 × 0.10 × 0.10
Crystal system	Monoclinic	Triclinic
Cell constants:		
a (Å)	14.8637(3)	8.7707(2)
b (Å)	6.9544(1)	9.3310(3)
c (Å)	19.6783(5)	17.9093(7)
α (°)		83.781(3)
β (°)	100.081(2)	85.626(2)
γ (°)		84.822(2)
V (Å^3)	2002.70(7)	1447.84(8)
Space group	$C2/c$	$P\bar{1}$
Z	2	1
D_c (g·cm^{-3})	2.409	2.478
F(000)	1416	1048
μ(MoKa)	2.167	2.230
Temp. (K)	173(2)	173(2)
Independent reflections ($I > 2\sigma(I)$)	1622	4549
Reflections collected/unique/R_{int}	5331 / 1932 / 0.0219	13127 / 5575 / 0.0238
Data/restraints/parameters	1932 / 3 / 149	5575 / 12 / 430
θ range (°)	2.78～26.00	2.20～26.00
Goodness-of-fit on F^2	1.091	1.041
$\Delta/\sigma)_{max}$	0.002	0.002
R[a], wR ($I > 2\sigma(I)$) [b]	0.0283, 0.0733	0.0234, 0.0584
R[a], wR[b] (all data)	0.0353, 0.0765	0.0311, 0.0602
w=1/[$\sigma^2(F_O^2)$ + aP^2 + bP], P=(F_o^2 + 2F_c^2)/3	a = 0.0480, b = 0.0000	a = 0.0343, b =0.0000
Largest diff. peak and hole (e·Å^{-3})	1.055, –0.775	0.943, –0.943

[a] $R = \Sigma||F_o| - |F_c||/\Sigma(|F_o|)$, [b] $wR = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for 1

Bond	Dist.	Bond	Dist.	Bond	Dist.
Mo(1)–O(1)	1.926(3)	Mo(1)–O(4)	2.238(3)	Mo(1)–O(7)	1.702(3)
Mo(1)–O(2)	2.238(2)	Mo(1)–O(6)	1.703(3)	Mo(1)–O(8)	1.900(1)
Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Mo(1)–O(2)	75.4(1)	O(2)–Mo(1)–O(4)	77.0(1)	O(4)–Mo(1)–O(7)	166.6(1)
O(1)–Mo(1)–O(4)	79.2(1)	O(2)–Mo(1)–O(6)	167.7(1)	O(4)–Mo(1)–O(8)	76.3(1)

O(1)–Mo(1)–O(6)	98.2(1)	O(2)–Mo(1)–O(7)	90.1(1)	O(6)–Mo(1)–O(7)	101.6(2)
O(1)–Mo(1)–O(7)	101.1(1)	O(2)–Mo(1)–O(8)	81.0(1)	O(6)–Mo(1)–O(8)	100.9(1)
O(1)–Mo(1)–O(8)	149.1(1)	O(4)–Mo(1)–O(6)	91.6(1)	O(7)–Mo(1)–O(8)	98.5(1)

Table 3. Selected Bond Lengths (Å) and Bond Angles (°) for 2

Bond	Dist.	Bond	Dist.	Bond	Dist.
Mo(1)–O(1)	1.963(2)	Mo(2)–O(13)	1.959(2)	Mo(3)–O(18)	1.704(2)
Mo(1)–O(2)	2.183(2)	Mo(2)–O(14)	1.699(2)	Mo(3)–O(19)	1.965(2)
Mo(1)–O(4)	2.336(2)	Mo(2)–O(15)	1.711(2)	Mo(4)–O(6)	1.961(2)
Mo(1)–O(11)	1.709(2)	Mo(2)–O(16)	1.889(2)	Mo(4)–O(7)	2.188(2)
Mo(1)–O(12)	1.717(2)	Mo(3)–O(5)	2.252(2)	Mo(4)–O(9)	2.349(2)
Mo(1)–O(13)	1.899(2)	Mo(3)–O(9)	2.290(2)	Mo(4)–O(19)	1.888(2)
Mo(2)–O(4)	2.295(2)	Mo(3)–O(16)	1.905(2)	Mo(4)–O(20)	1.727(2)
Mo(2)–O(10)	2.311(2)	Mo(3)–O(17)	1.696(2)	Mo(4)–O(21)	1.700(2)
Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Mo(1)–O(2)	73.87(9)	O(10)–Mo(2)–O(13)	77.15(8)	O(16)–Mo(3)–O(18)	98.2(1)
O(1)–Mo(1)–O(4)	78.27(9)	O(10)–Mo(2)–O(14)	84.0(1)	O(16)–Mo(3)–O(19)	150.3(1)
O(1)–Mo(1)–O(11)	105.8(1)	O(10)–Mo(2)–O(15)	171.7(1)	O(17)–Mo(3)–O(18)	103.5(1)
O(1)–Mo(1)–O(12)	92.4(1)	O(10)–Mo(2)–O(16)	81.69(9)	O(17)–Mo(3)–O(19)	99.3(1)
O(1)–Mo(1)–O(13)	145.81(9)	O(13)–Mo(2)–O(14)	99.1(1)	O(18)–Mo(3)–O(19)	96.6(1)
O(2)–Mo(1)–O(4)	76.20(8)	O(13)–Mo(2)–O(15)	98.2(1)	O(6)–Mo(4)–O(7)	74.67(9)
O(2)–Mo(1)–O(11)	91.6(1)	O(13)–Mo(2)–O(16)	148.21(9)	O(6)–Mo(4)–O(9)	77.59(8)
O(2)–Mo(1)–O(12)	162.0(1)	O(14)–Mo(2)–O(15)	103.7(1)	O(6)–Mo(4)–O(19)	144.7(1)
O(2)–Mo(1)–O(13)	83.93(9)	O(14)–Mo(2)–O(16)	102.0(1)	O(6)–Mo(4)–O(20)	92.4(1)
O(4)–Mo(1)–O(11)	165.64(9)	O(15)–Mo(2)–O(16)	99.5(1)	O(6)–Mo(4)–O(21)	105.2(1)
O(4)–Mo(1)–O(12)	89.9(1)	O(5)–Mo(3)–O(9)	79.09(8)	O(7)–Mo(4)–O(9)	77.88(8)
O(4)–Mo(1)–O(13)	71.29(9)	O(5)–Mo(3)–O(16)	81.75(9)	O(7)–Mo(4)–O(19)	82.48(9)
O(11)–Mo(1)–O(12)	103.5(1)	O(5)–Mo(3)–O(17)	88.8(1)	O(7)–Mo(4)–O(20)	161.1(1)
O(11)–Mo(1)–O(13)	100.3(1)	O(5)–Mo(3)–O(18)	167.4(1)	O(7)–Mo(4)–O(21)	92.8(1)
O(12)–Mo(1)–O(13)	102.6(1)	O(5)–Mo(3)–O(19)	78.21(9)	O(9)–Mo(4)–O(19)	71.49(9)
O(4)–Mo(2)–O(10)	78.36(7)	O(9)–Mo(3)–O(16)	83.24(9)	O(9)–Mo(4)–O(20)	86.0(1)
O(4)–Mo(2)–O(13)	71.27(9)	O(9)–Mo(3)–O(17)	166.0(1)	O(9)–Mo(4)–O(21)	169.3(1)
O(4)–Mo(2)–O(14)	161.4(1)	O(9)–Mo(3)–O(18)	88.3(1)	O(19)–Mo(4)–O(20)	101.8(1)
O(4)–Mo(2)–O(15)	93.6(1)	O(9)–Mo(3)–O(19)	71.62(8)	O(19)–Mo(4)–O(21)	102.4(1)
O(4)–Mo(2)–O(16)	81.47(9)	O(16)–Mo(3)–O(17)	102.0(1)	O(20)–Mo(4)–O(21)	104.0(1)

3 RESULTS AND DISCUSSION

3. 1 Synthesis

Syntheses of the dimeric and tetrameric molybdenum complexes depend mainly on pH value, molar ratio of molybdate to malate, and cations. Potassium molybdate and *R*,*S*-malic acid in the ratio of Mo(VI):mal = 1:1 reacted in aqueous solution at autogenous pH (pH = 4.8) at 70 °C to give *meso* malate molybdate **1**. In fact, **1** could be also obtained with a small excess of malic acid (even at 1:2 Mo:mal) at any pH between 4.8 and 5.8, using either KOH (5.0 M) or diluted HCl as required to maintain the pH value. Furthermore, when an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and malic acid (Mo:mal = 1:1.2～1:1.5) was allowed to react at pH 5.5～6.0 by adding KOH solution, it also led to **1**. However, it was surprising that when $NH_3\cdot H_2O$ instead of KOH was used, **1** was not obtained but only $(NH_4)_4[Mo_4O_{11}(R/S\text{-mal})_2]\cdot 6H_2O$[31] or $(NH_4)_4[MoO_2(S\text{-mal})_2][MoO_2(R\text{-mal})_2]$[34] was formed. The reaction of $K_2MoO_4\cdot 5H_2O$, malic acid and imidazole in a ratio of Mo:mal:im = 4:2:1, wherein diluted HCl was used to maintain the pH 3.0～4.0, led to a *meso* tetrameric complex with mixed cations **2**. It is noted that the reaction of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ with *R,S*-malic acid in 2:1 mol ratio resulted in the formation of enantiomers: either$(NH_4)_4[Mo_4O_{11}(R\text{-mal})_2]\cdot 6H_2O$ **3** or $(NH_4)_4[Mo_4O_{11}(S\text{-mal})_2]\cdot 6H_2O$ **4**[31] as individual crystals. Moreover, the bulk crystal of the

product showed optical rotation. Considering the similar conditions in preparing **2**, **3**, and **4**, their different configurations (mesomer **2**, enantiomer **3** or **4**) may be caused by the cation.

3. 2 Structure description

Fig. 1 shows the ORTEP plot of anion in **1**. The anion structure of **2** is given in Fig. 2. The molybdenum atoms in the two complexes are six-coordinated in an approximately octahedral geometry. The two malates coordinate tridentately *via* its *α*-alkoxy, *α*-carboxy and *β*-carboxy groups. **1** represents the first example of a structurally characterized dimeric 1:1 molybdenum-malate complex. The malate exhibits a similar coordination mode like citrate to the molybdenum[37], which has one less *β*-carboxy group than citrate. But malate formed 1:1 molybdenum malate complex more difficultly. The attempt to isolate monomeric complex with tridentate coordination like citrate molybdate $K_4[MoO_3(cit)]\cdot 2H_2O$ (H_4cit = citric acid) was unsuccessful[37].

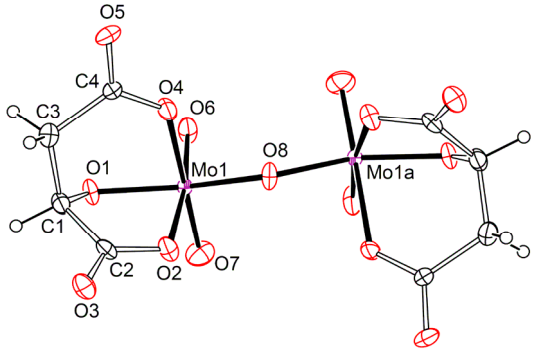

Fig. 1. ORTEP plot of the anion structure $[(Mo_AO_2)_2O(R\text{-mal})_2]^{4-}$ in 1 at 30% probability thermal ellipsoids

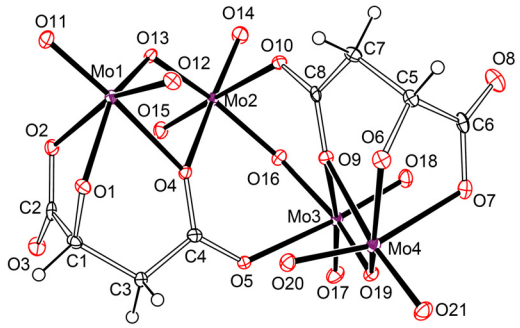

Fig. 2. ORTEP plot of the anion stucture $[(Mo_AO_2)_4O_3(R\text{-mal})_2]^{4-}$ in 2 at 30% probability thermal ellipsoids

All Mo–O distances in complexes **1** and **2** vary systematically according to their bond types. The O=Mo=O angles (101.6(2) ~ 104.0(1)°) are considerably larger than the regular octahedral value of 90° for the *cis*-dioxo configuration arising from the oxygen-oxygen repulsions associated with short Mo=O bond lengths (1.696(2)~1.727(2) Å). The Mo–O distances in Mo–O–Mo bridges range from 1.888(2) to 1.965(2) Å. The Mo–O (*α*-alkoxy) bonds (mean 1.950(2) Å) are slightly shorter, and Mo–O (*α*-carboxy) (2.183(2) to 2.238(2) Å) are comparable to the respective linkages (*i.e.*, 1.996~2.035 and 2.167~2.206 Å, respectively) in coordinated homocitrate in MoFe protein and its putative transitionstate complex[38, 39]. The Mo–O (*β*-carboxy) bond lengths in the overall range of 2.238(3)~2.349(2) Å are the longest of all, showing weak coordination of *β*-carboxy group to Mo. For comparison, some related Mo–O bond distances of malato, citrato and homocitrato molybdates are listed in Table 4. In these dimeric and tetrameric molybdates, the bond distances of α-alkoxy to molybdenum in **2** are shorter than those of *α*-carboxy group to molybdenum. However, the difference between Mo–O (*α*-carboxy) and Mo–O (*β*-carboxy) bond distances is smaller. Especially, the bond distance of Mo–O (*β*-carboxy) is the same as that of Mo–O (*α*-carboxy) in **1**, indicating the *β*-carboxy group has comparable coordination ability. Moreover, there are extended hydrogen bonds in **1** and **2** for water molecules and imidazole cations, and some strong hydrogen bonds like O(1w)···O(5a) 2.702(4) Å and O(1w)···O(6b) 2.826(5) Å in **1** (*a* 2.5 – *x*, –½ + *y*, 1.5 – *z*; *b* 2.5 – *x*, ½ + *y*, 1.5 – *z*), and O(1w)···O(1) 2.706(3) Å, O(2w)···O(3wa) 2.841(4) Å, O(3w)···O(20a) 2.703(4) Å and O(4w)···O(10) 2.771(4) Å in **2** (*a* 1 – *x*, –*y*, 1 – *z*; *b* 1 – *x*, 1 – *y*, 2 – *z*).

3. 3 NMR spectroscopy

The solution ^{13}C and ^{1}H NMR spectra of complexes **1** and **2** were measured in D_2O. **2** shows one set of clean ^{13}C and ^{1}H NMR signals, while **1** developes corresponding ^{13}C and ^{1}H signals of other

related complexes during data accumulation that makes spectra progressively complicated in each region. ^{13}C NMR spectra of **1** and **2** are shown in Figs. 3 and 4, respectively. In comparison with the corresponding carbons in malic acid (^{13}C NMR δ_C (400 M, D_2O) ppm: 179.1 $(CO_2)_\alpha$, 177.1 $(CO_2)_\beta$, 69.4 (≡CO), 41.0 (=CH_2)), **2** shows large downfield shifts of the ^{13}C resonances. The shifts of α-alkoxy carbon ($\Delta\delta$ 12.8 ppm) at 82.2 ppm, α-carboxy carbon ($\Delta\delta$ 7.3 ppm) at 186.4 ppm, and β-carboxy carbon ($\Delta\delta$ 4.9 ppm) at 182.0 ppm indicate that the three groups in malic acid coordinate to the molybdenum atom simultaneously. The solution NMR spectrum indicates that the tetrameric structure of the anion is retained in aqueous solution. However, Fig. 4 for **2** shows only one set of clean ^{13}C NMR spectrum, and Fig. 3 for **1** illustrates three sets of ^{13}C NMR signals. The peaks at 187.7, 181.2, 84.7 and 41.3 ppm can be respectively assigned to the resonances of α-carboxy, β-carboxy, α-alkoxy and methylene carbons for the coordinated malate ligands of the dimeric anion in **1**. The other two sets of peaks belong to other species. One (186.4, 182.1, 82.2, and 42.3 ppm) is comparable with that of ^{13}C NMR spectra of **2** (186.4, 182.0, 82.2, and 42.3 ppm). The resonances are attributed to the coordinated malate in the tetrameric malate molybdate **2**. The other set (187.5, 181.3, 85.6, and 43.7 ppm) might belong to malato molybdenum complex like 1:2 (Mo:mal) species, which suggests the following equilibrium in solution.

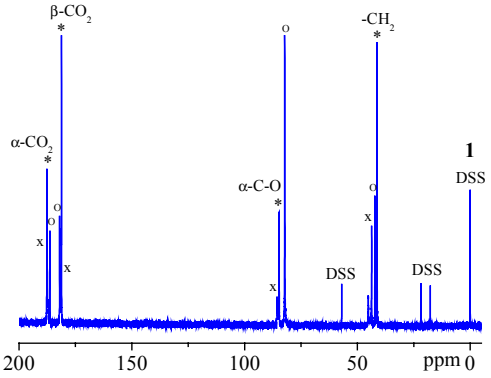

Fig. 3. ^{13}C NMR spectrum of complex 1. Labels: dimeric molybdenum malate complex (∗); tetrameric molybdenum malate complex (o); other molybdenum malate complex (x)

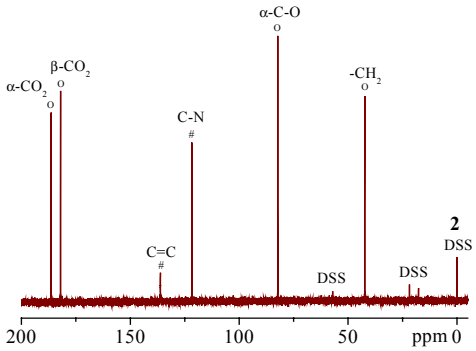

Fig. 4. ^{13}C NMR spectrum of complex 2. Labels: tetrameric molybdenum malate complex (o); imidazole (#)

$$3[(MoO_2)_2O(mal)_2]^{4-} \leftrightarrows [(MoO_2)_4O_3(mal)_2]^{4-} + 2[MoO_2(mal)_2]^{4-}$$

The ^1H NMR spectrum of **2** shows one set of signals of coordinated malate, indicating it is stable in aqueous solution. This observation is in agreement with the conclusion derived from the ^{13}C NMR spectrum of **2**. The ^1H NMR spectrum of **1** shows two sets of multiplets. The main body of peaks belongs to the coordinated malate in dimeric malate molybdenum **1**. The minor set of peaks, similar to the ^1H NMR spectrum of **2**, was attributed to tetrameric molybdenum complex **2**. The ^1H NMR spectrum of **1** indicated that the dimeric malate molybdate decomposed and formed some other malate molybdenum species, like tetrameric molybdenum complex.

3. 4 IR spectroscopy

The FT-infrared spectra of complexes **1** and **2** display characteristic features of coordinated malate ligand. The antisymmetric stretching carboxy vibra-

tions ν_{as}(COO) of the complexes all shift to lower frequency compared to that of free malic acid. The corresponding symmetric stretching vibrations ν_s(COO) appeared at 1433～1363 cm^{-1} for the two compounds. In the region around 900 cm^{-1}, the complexes show several bands resulting from *cis*-dioxo molybdenum. Additional bands in the 801～504 cm^{-1} range can be assigned to ν_{as}(Mo–O–Mo) and ν_s(Mo–O–Mo) bridges.

4 CONCLUSION

The structures of the title compounds are strongly influenced by pH value, metal-ligand molar ratio, and counterions. The ^{13}C and ^{1}H NMR spectra of complex **1** indicate that the dimeric structure dissociated partly in solution into tetrameric and other coordinated species. To our surprise, the malates from the decomposition of **1** still coordinate to molybdenum like 2:1 species (Mo:mal), which is different from molybdenum citrate complex which dissociates to free uncoordinated citrate in solution[43]. However, the NMR spectra of **2** show only one set of resonances of the coordinated malate, indicating it is stable and retains its tetrameric structure in solution without any dissociation.

Table 4. Comparisons of Mo–O Distances (Å) in Hydroxycarboxylato Molybdates (H_4homocit = Homocitric Acid)

Complex	Mo─$O_{\alpha\text{-alkoxy}}$	Mo─$O_{\alpha\text{-carboxy}}$	Mo─$O_{\beta\text{-carboxy}}$	Ref.
$K_8[(MoO_2)_2O(R\text{-mal})_2][(MoO_2)_2O(S\text{-mal})_2]\cdot 4H_2O$ **1**	1.926(3)	2.238(2)	2.238(3)	This work
$K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$	1.958(3)	2.210(3)	2.276(3)	[37]
$K_2Na_4[(MoO_2)_2O(cit)_2]\cdot 5H_2O$	1.929(3), 1.958(3)	2.218(3), 2.197(4)	$2.264(3)_{av}$	[40]
Average	1.943(3)	2.216(3)	2.260(3)	
$(Him)_2K_6[(MoO_2)_4O_3(R\text{-mal})_2][(MoO_2)_4O_3(S\text{-mal})_2]\cdot 8H_2O$ **2**	1.963(2), 1.961(2)	2.183(2), 2.188(2)	$2.314(2)_{av}$, $2.297(2)_{av}$	This work
$(NH_4)_4[Mo_4O_{11}(R\text{-mal})_2]\cdot 6H_2O$	1.925(6)	2.226(6)	$2.296(5)_{av}$	[31]
$K_4[(MoO_2)_4O_3(Hcit)_2]\cdot 6H_2O$	1.976(5), 1.968(5)	2.185(5), 2.211(5)	$2.310_{av}(5)$, $2.357_{av}(5)$	[41]
$K_2(NH_4)_2[(MoO_2)_4O_3(R,S\text{-Hhomocit})_2]\cdot 6H_2O$	1.929(4), 1.955(4)	2.194(4), 2.181(4)	$2.311_{av}(4)$, $2.309_{av}(4)$	[42]
$K_5[(MoO_2)_4O_3(R,S\text{-Hhomocit})_2]Cl\cdot 5H_2O$	1.947(3), 1.931(3)	2.193(3), 2.200(3)	$2.280_{av}(3)$, $2.314_{av}(3)$	[42]
Average	1.951(4)	2.196(4)	2.310(3)	
Azotobacter vinelandii (Av1)	1.996	2.167		[38]
Clostridium pasturianum (Cp1)	2.035	2.206		[39]

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